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# Bioinspired Surface Treatments for Improved Decontamination: Additional POSS Treatments

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## EXECUTIVE SUMMARY

The Center for Bio/Molecular Science and Engineering at the Naval Research Laboratory (NRL) initiated a program in January 2015 for evaluation of bioinspired treatments suitable for use as a top coat on painted surfaces with the intention of achieving improved aqueous decontamination of these materials. Funding was provided by the Defense Threat Reduction Agency (DTRA, CB10125). This report details results for evaluation of polyhedral oligomeric silsesquioxane (POSS) surface treatments. POSS are cage structures of silicon and oxygen that bind to organic polymers producing chains that can serve to reinforce the overall structure. Previous reports (NRL/MR/6930--18-9775) addressed an initial set of POSS treatments and allowed identification of promising approaches for improving performance in the POSS topcoats (NRL/MR/6930--18-9826). The coatings evaluated under the current study included POSS cage structures with iso-octyl side chains with (SO1455) and without (MS0805) a fluorinated group. This fluorinated group (Optool) was also considered alone and as a multipoint modification on a POSS cage (MS0860 Optool). The materials were deposited on polyurethane paint coated aluminum coupons. Retention of the simulants paraoxon, methyl salicylate, dimethyl methylphosphonate, and diisopropyl fluorophosphate following treatment of contaminated surfaces with a soapy water solution is reported along with droplet diffusion on the surfaces and wetting angles.

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# **BIOINSPIRED SURFACE TREATMENTS FOR IMPROVED DECONTAMINATION: ADDITIONAL POSS TREATMENTS**

## **INTRODUCTION**

The DoD Chemical and Biological Defense Program (CBDP) seeks to provide technologies for protection of forces in a contaminated environment, including those for contamination avoidance, individual protection, collective protection, and decontamination. In January 2015, the Center for Bio/Molecular Science and Engineering at the Naval Research Laboratory (NRL) began an effort funded through the Defense Threat Reduction Agency (DTRA, CB10125) intended to evaluate and develop top-coat type treatments suitable for application to painted surfaces that would reduce retention of chemical threat agents following standard decontamination approaches. The effort sought to survey relevant and related areas of research and evaluate identified technologies under appropriate methods to determine efficacy, scalability, and durability. The current document summarizes results for one of the identified technologies. In this case, a series of polyhedral oligomeric silsesquioxanes (POSS) prepared by Hybrid Plastics Inc. This series of materials was selected/designed based on lessons learned from two prior sets of evaluations. That work was summarized in NRL/MR/6930--18-9775 and NRL/MR/6930--18-9826.[1, 2]

POSS treatments were initially evaluated as an alternative for achieving the behaviors noted for slippery liquid-infused porous surfaces (SLIPS)[3-10] or slippery omniphobic covalently attached liquids (SOCAL),[11, 12] while avoiding the durability issues noted for those materials. Polyhedral oligomeric silsesquioxanes (POSS) are cage structures of silicon and oxygen that bind to organic polymers providing molecular level reinforcement. They are used to enhance the mechanical properties of polymers (scratch resistance or increased modulus, for example) and thermal stability. They can also be used as flow aids, dispersants, lubricants, and surface modifiers. They have been considered previously for control of corrosion in automotive and aerospace applications.[13]

The POSS variants of the initial study[1] included a cage structure with methacrylate side chain (MA0702), two variants using a cage structure with methoxylated polyethylene glycol side chain (PG1192 and PG1193), two variants using the Corin XLS polyimide structure (Corin XLS and Corin 0578) and two cage structures with alkyl groups of varied length (SO1450 and SO1455; Figure 1). These initial POSS treatments provided interesting results with wetting and target retention behaviors varying widely across the coating types. Different coatings provided better resistance to retention of individual targets, but no material provided dramatically improved overall performance. Highlights of those results indicated the potential of the FL0578 as a mobile lubricant as well as generally better performance in the PG1193 and SO1455 coatings.

The follow-on study utilized materials identified based on those initial promising results, including three materials with isooctyl side chains (AM0270, MA0719, and TH1555) as well as a fluorinated structure (SO1465; Figure 1). The materials provided significantly improved performance over both the painted surface and the materials of the original study. It was proposed that additional improvements in performance could be obtained through combining a structure similar to the SO1465 of that study or the SO1455 of the original study with an alkane or fluoroalkyl group at the open corner position. The MS0805 structure currently available in the Hybrid Plastics catalog was suggested (Figure 2). In addition to enhanced performance, this second series of POSS samples addressed the damage noted on repeated use of the original materials. The isooctyl materials did not show evidence of damage during processing.

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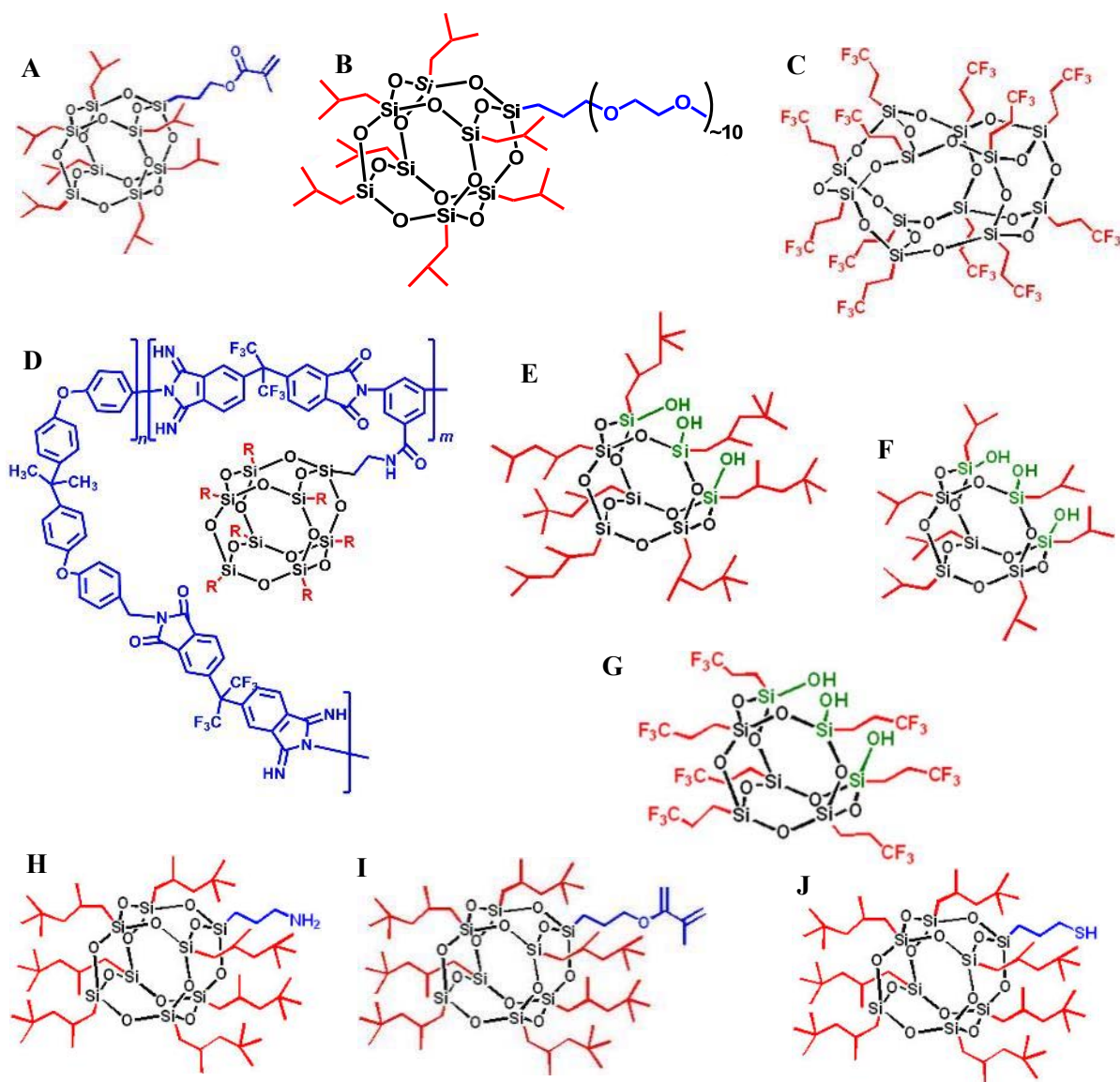


Fig. 1 — Molecular structures for the initial POSS variants: methacryloisobutyl POSS (A; MA0702); methoxyPEGisobutyl POSS (B; PG1192); trifluoropropyl POSS (C; FL0578); Corin XLS Polyimide (D); trisilanolisocetyl POSS (E; SO1455); trisilanolisobutyl POSS (F; SO1450); hepta-trifluoropropyl trisilanol POSS (G; SO1465) aminopropylisooctyl POSS (H; AM0270); methacryloisooctyl POSS (I; MA0719); and mercaptopropylisooctyl POSS (J; TH1555).[1, 2]

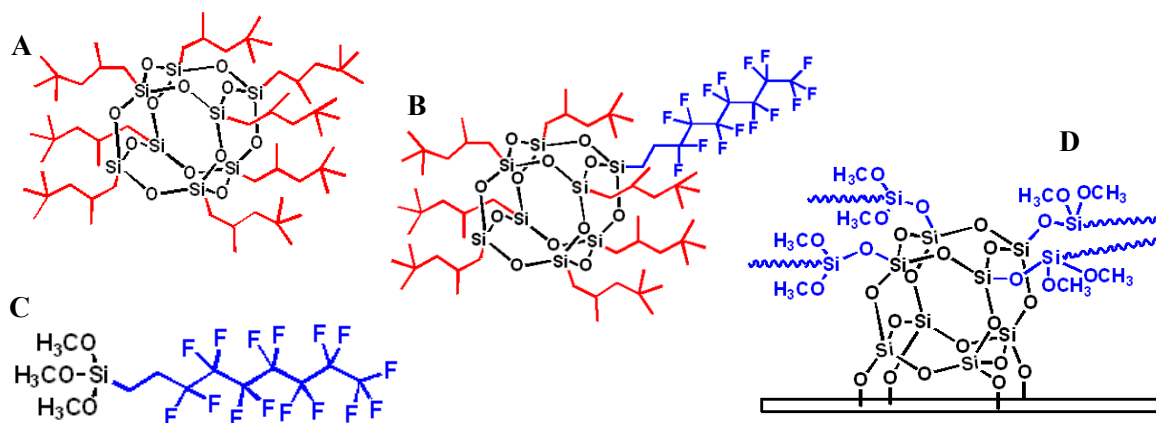


Fig. 2 — Molecular structures for the new coating variants: iOcytyl POSS (A; MS0805); iOcytyl F POSS (B; SO1455F); Optool (C); MS0860 + Optool (D). In D, the blue components are the fluorinated Optool group.

In addition to the identified isooctyl bearing MS0805 structure (Figure 2), the current study considered deposition variations. Painted coupons were modified through neat application of the structure as well as application of the material in a solvent preparation (ethyl acetate). A fluorinated isooctyl bearing POSS variant was also considered here (SO1455F; Figure 2); this material was similarly applied both neat and as an ethyl acetate solution. Finally, a POSS cage was modified with the Optool group (Figure 2) to provide surface binding, fluorination, and a degree of roughness to the coating. Coupons were also modified using Optool alone for comparison. For the complete system evaluated under this study, aluminum coupons were coated with a polyurethane paint system by NRL and were provided to Hybrid Plastics Inc (Figure 3). Following deposition of the POSS variants, coupons were returned to NRL for evaluation using standard approaches including measurement of sessile, sliding, and shedding contact angles and quantification of retention for the simulant compounds.

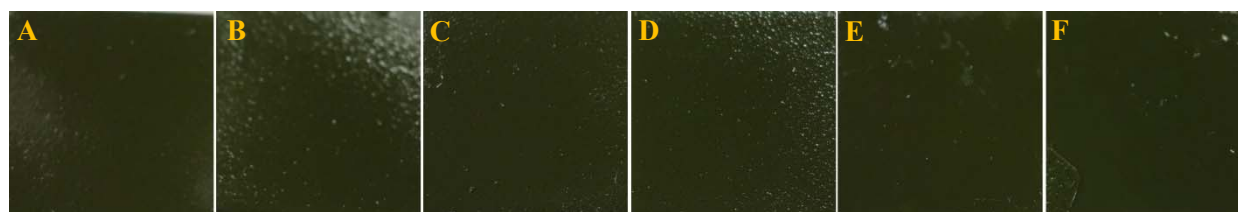


Fig. 3 — Images of painted coupons with hepta-trifluoropropyl trisilanol POSS (A; MS0805 neat) aminopropylisooctyl POSS (B; MS0805 solvent); methacrylisooctyl POSS (C; SO1455F neat); and mercaptopropylisooctyl POSS (D; SO1455F solvent); (E; OPTool); (F; MS0860 OPTool).

## METHODS

Sessile contact angles for samples evaluated under this effort used three 3  $\mu\text{L}$  droplets per surface with each droplet measured independently three times for each of three targets, water, ethylene glycol, and *n*-heptane. Geometric surface energy was calculated based on the water and ethylene glycol interactions using software designed for the DROPimage goniometer package. Sliding angles were determined using 5  $\mu\text{L}$  droplets. The droplet was applied at 0° after which the supporting platform angle was gradually increased up to 60°. Sliding angles for each of the liquids were identified as the angle for which movement of the droplet was identified. Shedding angles for each liquid were determined using 12  $\mu\text{L}$  droplets initiated 2.5 cm above the coupon surface. Changes in base angle of 10° were utilized to identify the range

of droplet shedding angle based on a complete lack of droplet retention by the surface (not sliding). The angle was then reduced in steps of  $1^\circ$  to identify the minimum required angle. Droplet diameters were determined using tools provided by Adobe Photoshop CS3. Droplets of  $5\ \mu\text{L}$  were applied to the surfaces and images were collected at 30 s intervals for 5 min followed by images at 5 min intervals for a total of 30 min. DFP samples were kept covered for the duration of the experiment to minimize evaporation. In some cases, reflections from the glass cover can be seen in the images.

Simulant exposure and evaluation methods were based on the tests developed by Edgewood Chemical Biological Center referred to as Chemical Agent Resistance Method (CARM).[14] Standard target exposures utilized a challenge level of  $10\ \text{g}/\text{m}^2$ . The painted coupons were  $0.00101\ \text{m}^2$ ; the  $10\ \text{g}/\text{m}^2$  target challenge was applied to the surfaces as two equally sized neat droplets. Following application of the target, coupons were aged 1 h prior to use of a gentle stream of air to expel target from the surface. Samples were then rinsed with soapy water ( $0.59\ \text{g}/\text{L}$  Alconox in deionized water). The rinsed coupons were soaked in isopropanol for 30 min to extract remaining target; this isopropanol extract was analyzed by the appropriate chromatography method to determine target retention on the surface.

For paraoxon, methyl salicylate (MES), diisopropyl fluorophosphate (DFP), and dimethyl methylphosphonate (DMMP) analysis, gas chromatography-mass spectrometry (GC-MS) was accomplished using a Shimadzu GCMS-QP2010 with AOC-20 auto-injector equipped with a Restex Rtx-5 ( $30\ \text{m} \times 0.25\ \text{mm ID} \times 0.25\ \mu\text{m df}$ ) cross bond 5% diphenyl 95% dimethyl polysiloxane column. A GC injection temperature of  $200^\circ\text{C}$  was used with a 1:1 split ratio at a flow rate of  $3.6\ \text{mL}/\text{min}$  at  $69.4\ \text{kPa}$ . The oven gradient ramped from  $50^\circ\text{C}$  (1 min hold time) to  $180^\circ\text{C}$  at  $15^\circ\text{C}/\text{min}$  and then to  $300^\circ\text{C}$  at  $20^\circ\text{C}/\text{min}$  where it was held for 5 min.

## RESULTS

Analysis of the support surface in the absence of additional coatings provides a point of comparison for evaluating the benefits of the surface treatments. Each table includes data on the relevant support material, a painted aluminum coupon and for a Fomblin Y lubricated painted aluminum coupon. Results for AM0270 and TH1555, materials considered under the previous POSS evaluation, are also included for comparison. Application of the coatings considered here reduced the surface energy of the painted surface (Table 1 and Figure 4). The fluorinated isooctyl structure (SO1455F) yielded the lowest surface energy with wetting behaviors similar to those of the MA0702 of the original study. All of the SO1455F and MS0805 POSS surfaces were fully wetted by heptane. The Optool and MS0860 Optool surfaces yielded heptane contact angles of  $\sim 32^\circ$ . No sliding on the surfaces was noted below an incline of  $60^\circ$ . Shedding of ethylene glycol was noted for the SO1455F surfaces at  $\sim 45^\circ$ ; no other shedding behavior was noted for these surfaces.

The tendency of droplets to spread across the surfaces was also evaluated (Figure 5; Appendices). For these studies, droplets of the simulants ( $5\ \mu\text{L}$ ) were utilized. The spread of the droplets was quantified by measuring the diameter of the droplets in the images over time (Figure 6). For the paint only samples, MES and DFP spread quickly, reaching the edges of the coupon at 10 and 2 min, respectively. DMMP does not spread during the course of the 30 min incubation. The coatings considered here produced differing results. DMMP spread was negligible in all cases; application of Fomblin Y had a negative impact on this behavior. No spread was noted for any target on the Optool or MS0860 Optool surfaces. MES spread was significantly reduced by the SO1455F coating both under neat and solvent application. MS0805 had a less dramatic impact but did reduce spread as compared to the painted surface. The impact of the coatings on DFP spread was more complicated. For neat deposition of SO1455F and MS0805, the DFP droplet initially spread on the surface and then became unobservable. Penetration into the surface was suspected, but this was not supported by retention studies. For the solvent based depositions, the more typical behavior was

observed, with MS0805 yielding slight improvements over Fomblin Y lubrication and more significant reductions noted for the SO1455F surface.

Table 1 – Sessile, Sliding, and Shedding Contact Angles on Aluminum Supports

Coupon	Liquid	Sessile Angle	Sliding Angle	Shedding Angle	Geometric Surface Energy (mJ/m <sup>2</sup> )
Paint Only	water	47.5 ± 1.1	>60	>60	71.9 ± 5.1
	ethylene glycol	55.7 ± 2.1	>60	>60	
	n-heptane	--	--	--	
Fomblin Y Oiled Paint	water	73.1 ± 2.1	>60	46.7 ± 3.3	32.2 ± 1.6
	ethylene glycol	52.5 ± 0.61	>60	49.8 ± 4.9	
	n-heptane	40.1 ± 2.9	>60	36.6 ± 3.3	
AM0270	water	77.7 ± 1.5	>60	>60	30.4 ± 1.9
	ethylene glycol	56.7 ± 2.0	>60	>60	
	n-heptane	--	--	--	
TH1555	water	84.7 ± 0.7	>60	>60	41.4 ± 2.9
	ethylene glycol	48.9 ± 1.9	>60	>60	
	n-heptane	--	--	--	
<b>New POSS Treatments</b>					
MS0805 (neat)	water	75.9 ± 0.6	>60	>60	28.2 ± 0.5
	ethylene glycol	63.6 ± 0.7	>60	>60	
	n-heptane	--	--	--	
MS0805 (solvent)	water	79.1 ± 0.8	>60	>60	26.5 ± 0.4
	ethylene glycol	62.0 ± 0.6	>60	>60	
	n-heptane	--	--	--	
SO1455F (neat)	water	85.2 ± 0.7	>60	>60	21.7 ± 0.3
	ethylene glycol	71.9 ± 0.5	>60	44.8 ± 0.4	
	n-heptane	--	--	--	
SO1455F (solvent)	water	85.9 ± 0.7	>60	>60	21.1 ± 0.5
	ethylene glycol	73.1 ± 0.9	>60	42.0 ± 1.7	
	n-heptane	--	--	--	
OPtool	water	88.1 ± 1.6	>60	>60	33.7 ± 3.3
	ethylene glycol	97.0 ± 2.5	>60	>60	
	n-heptane	32.3 ± 0.4	>60	>60	
MS0860 OPtool	water	90.1 ± 0.9	>60	>60	25.9 ± 2.3
	ethylene glycol	92.1 ± 0.7	>60	>60	
	n-heptane	32.1 ± 0.7	>60	>60	

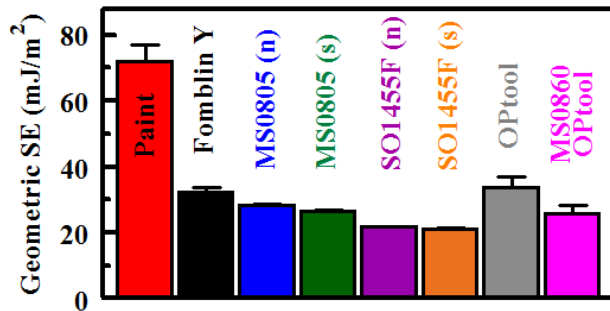


Fig. 4 — Geometric surface energy (mJ/m<sup>2</sup>) for the evaluated coatings. PG1193 was fully wetted by water and heptane preventing calculation of values for these surfaces.

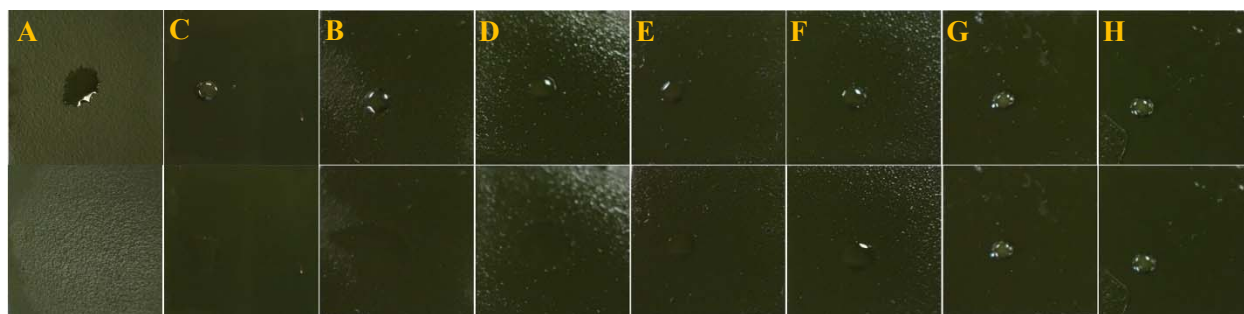


Fig. 5 — Images of coupons at 0 and 30 min following MES exposure: painted coupon (A) and painted coupon with Fomblin Y (B), MS0805 neat (C), MS0805 solvent (D), SO1455F neat (E), SO1455F solvent (F), Optool (G), MS0860 Optool (H).

The coupons were subjected to several cycles of simulant exposure ( $10 \text{ g/m}^2$ ), aging, washing, and drying over a period of three weeks (Figure 5). While the initial POSS coatings showed significant damage, these materials showed little change in the appearance or wetting characteristics over these processing steps. When the soapy water process was employed (Figure 7; Table 2), retention of all targets was less for the Fomblin Y lubricated paint than for the paint only surface. Neat application of the SO1455F and MS0806 coatings resulted in increased retention of DFP and MES retention similar to that of the Fomblin Y surface. Solvent application of these coatings, on the other hand, provided reductions in retention for all targets over painted surfaces with all retention at or below  $0.5 \text{ g/m}^2$ . The Optool and MS0860 Optool coatings reduced paraoxon retention below the detection threshold for the instrument. Retention of all other compounds was less than  $0.3 \text{ g/m}^2$ .

For comparison, paint only coupons retained significant amounts of target at  $5.48$ ,  $6.20$ ,  $4.28$ , and  $0.52 \text{ g/m}^2$ . When no rinsing or decontamination steps were used, paint only coupons retained the following: paraoxon –  $9.84 \text{ g/m}^2$ , MES –  $9.54 \text{ g/m}^2$ , DMMP –  $9.90 \text{ g/m}^2$ , DFP -  $7.39 \text{ g/m}^2$ . Though the nominal target application was  $10 \text{ g/m}^2$ , recovery from surfaces was always less than this value. Losses due to evaporation would be expected, especially for DFP. Additional losses likely occur during rinse steps due to agent interaction with the untreated region of the coupon; the back of these coupons is unpainted aluminum.

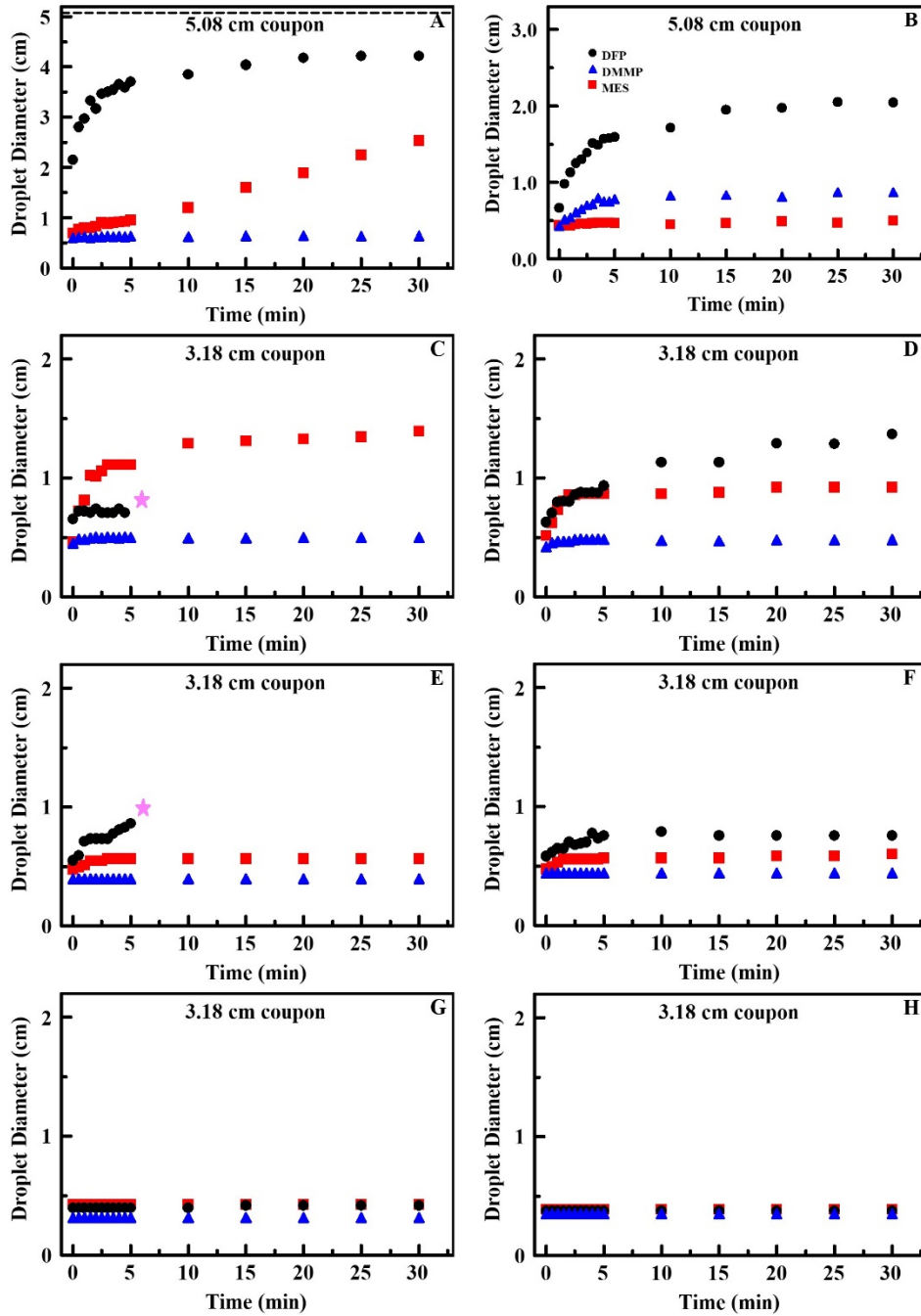


Fig. 6 — Droplet diameters over time following exposure to DFP (black), MES (red), and DMMP (blue) for a painted coupon (A) and painted coupons with Fomblin Y (B), MS0805 neat (C), MS0805 solvent (D), SO1455F neat (E), SO1455F solvent (F), Optool (G), and MS0860 Optool (H).

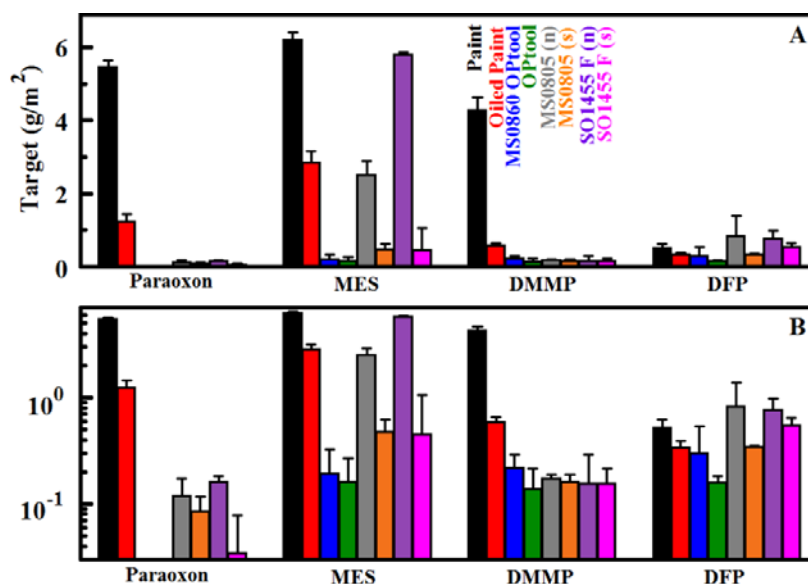


Fig. 7 — Target retention by coupons following treatment with an air stream and rinsing with soapy water shown on a linear scale (A) and (B) on a log scale: painted (black), Fomblin Y (red), MS0860 Optool (blue), Optool (green), MS0805 neat (gray), MS0805 solvent (orange), SO1455F neat (purple), and SO1455 solvent (pink).

Table 2 – Target Retention ( $\text{g}/\text{m}^2$ ) Following 1 h Aging on Aluminum Supports

Coupon	Paraoxon	MES	DMMP	DFP
Paint Only	5.48	6.20	4.28	0.52
Fomblin Y Oiled Paint	1.24	2.85	0.59	0.34
AM0270	0.08	0.43	0.16	0.51
TH1555	0.10	0.04	0.09	0.43
New Coatings Considered				
MS0805 neat	0.11	2.50	0.17	0.82
MS0805 solvent	0.09	0.48	0.16	0.34
SO1455F neat	0.16	5.81	0.16	0.77
SO1455 solvent	0.03	0.45	0.16	0.54
Optool	ND	0.16	0.14	0.16
MS0860 Optool	ND	0.19	0.22	0.30

ND = not detected

## CONCLUSIONS

The POSS samples of the earlier studies[1, 2] yielded interesting results with wetting and target retention behaviors varying widely across the POSS structures. Different coatings provided better resistance to retention of individual targets, but did not provide overall improved performance. The materials considered here were selected and designed based on that range of results. Here, the considered materials provided significantly improved performance over both the painted surface and the materials of the original study. The TH1555 and AM0270 POSS treatments of the second study on these materials [2] yielded retention behaviors similar to those noted for the MS0805 and SO1455F of the current study, with the new materials yielding lower surface energy. Here, MS0805 and SO1455F provide an effective demonstration of the potential impact of the deposition method, with solvent based application producing significantly better behaviors than those noted for application by neat deposition. The Optool variations used here also provided significant reductions in target retention. The coatings considered here did not show evidence of

damage during processing. Spectrophotometric analysis is necessary to determine the overall impact on color and reflectivity. It may also be of interest to consider the impact of outdoor aging on these materials.

## ACKNOWLEDGEMENTS

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## REFERENCES

1. White, B., Melde, B., Moore, M., and Malanoski, A., "Bioinspired Surface Treatments for Improved Decontamination: Polyhedral Oligomeric Silsesquioxanes (POSS)," US Naval Research Laboratory, Washington, DC, **2018**; NRL/MR/6930-18,9775.
2. White, B., Melde, B., Moore, M., Malanoski, A., and Lichtenhan, J.D., "Bioinspired Surface Treatments for Improved Decontamination: Improved POSS Treatments," US Naval Research Laboratory, Washington, DC, **2018**; NRL/MR/6930-18,9826.
3. Okada, I. and Shiratori, S., "High-Transparency, Self-Standable Gel-SLIPS Fabricated by a Facile Nanoscale Phase Separation," *ACS Applied Materials & Interfaces*, **2014**, 6, 1502-08.
4. Samaha, M.A. and Gad-el-Hak, M., "Polymeric Slippery Coatings: Nature and Applications," *Polymers*, **2014**, 6, 1266-311.
5. Wong, T.S., Kang, S.H., Tang, S.K.Y., Smythe, E.J., Hatton, B.D., Grinthal, A., and Aizenberg, J., "Bioinspired self-repairing slippery surfaces with pressure-stable omniphobicity," *Nature*, **2011**, 477, 443-47.
6. Xiao, L.L., Li, J.S., Mieszkina, S., Di Fino, A., Clare, A.S., Callow, M.E., Callow, J.A., Grunze, M., Rosenhahn, A., and Levkin, P.A., "Slippery Liquid-Infused Porous Surfaces Showing Marine Antibiofouling Properties," *ACS Applied Materials & Interfaces*, **2013**, 5, 10074-80.
7. White, B., Moore, M., Malanoski, A., and Campbell, C., "Bioinspired Surface Treatments for Improved Decontamination: Silicon and Latex Polymer SLIPS Treatments," US Naval Research Laboratory, Washington, DC, **2017**; NRL/MR/6930-17,9733.
8. White, B., Melde, B., Malanoski, A., and Moore, M., "Bioinspired Surface Treatments for Improved Decontamination: Silicate-Based Slippery Liquid-Infused Porous Surfaces (SLIPS)," US Naval Research Laboratory, Washington, DC, **2017**; NRL/MR/6930-17,9734.
9. White, B., Melde, B., Moore, M., Malanoski, A., Campbell, C., and Bryan, B., "Bioinspired Surface Treatments for Improved Decontamination: Textured Polyurethane for Slippery Liquid-Infused Porous Surfaces," US Naval Research Laboratory, Washington, DC, **2018**; NRL/MR/6930-18,9804.
10. White, B., Melde, B., Moore, M., and Malanoski, A., "Bioinspired Surface Treatments for Improved Decontamination: Polymer-Based Slippery Liquid-Infused Porous Surfaces (SLIPS)," US Naval Research Laboratory, Washington, DC, **2018**; NRL/MR/6930-18,9773.
11. Wang, L. and McCarthy, T.J., "Covalently Attached Liquids: Instant Omniphobic Surfaces with Unprecedented Repellency," *Angewandte Chemie International Edition*, **2016**, 55, 244-8.
12. White, B., Melde, B., Malanoski, A., and Moore, M., "Bioinspired Surface Treatments for Improved Decontamination: Slippery Omniphobic Covalently Attached Liquid (SOCAL)," US Naval Research Laboratory, Washington, DC, **2017**; NRL/MR/6930-17,9761.
13. Iacono, S., Vij, A., Peloquin, A., Yandek, G., Smith, D.J., and Mabry, J., "Fluorinated Polyhedral Oligomeric Silsesquioxanes (F-POSS)," US Air Force Research Laboratory, **2010**; AFRL-RZ-ED-TP-2010-070.
14. Lalain, T., Mantooth, B., Shue, M., Pusey, S., and Wylie, D., "Chemical Contaminant and Decontaminant Test Methodology Source Document," US Army RDEC, Edgewood Chemical Biological Center, Aberdeen Proving Ground, MD, **2012**; ECBC-TR-980.

**Appendix A****MS0805 (NEAT) COUPON IMAGES**

Fig. A1 — DFP on MS0805 (neat). Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1.0 (D), 1.5 (E), 2.0 (F), 2.5 (G), 3.0 (H), 3.5 (I), 4.0 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target. These images were collected with a glass cover in place to limit evaporation. Reflections from the cover can be seen in some images.

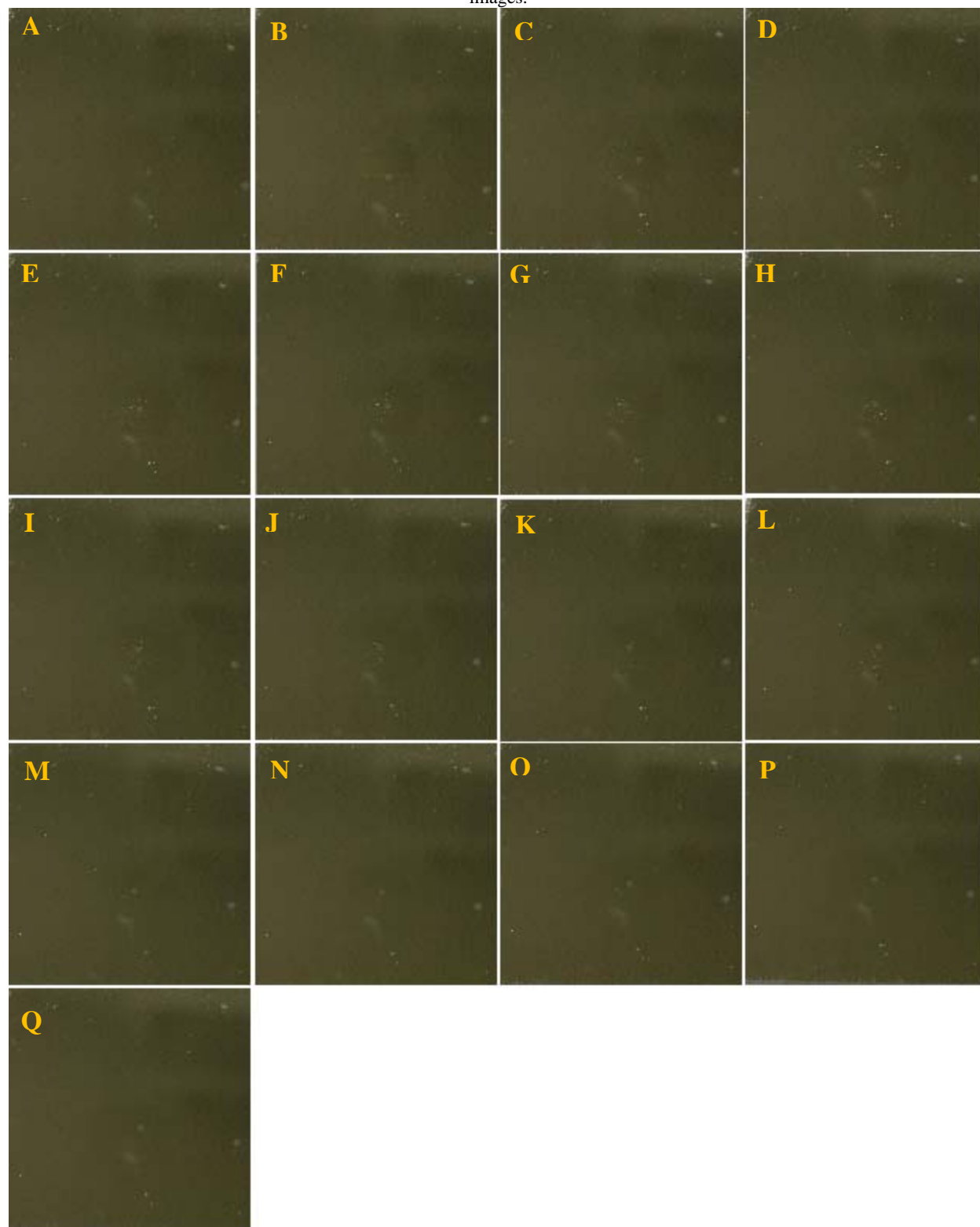


Fig. A2 — MES on MS0805 (neat). Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

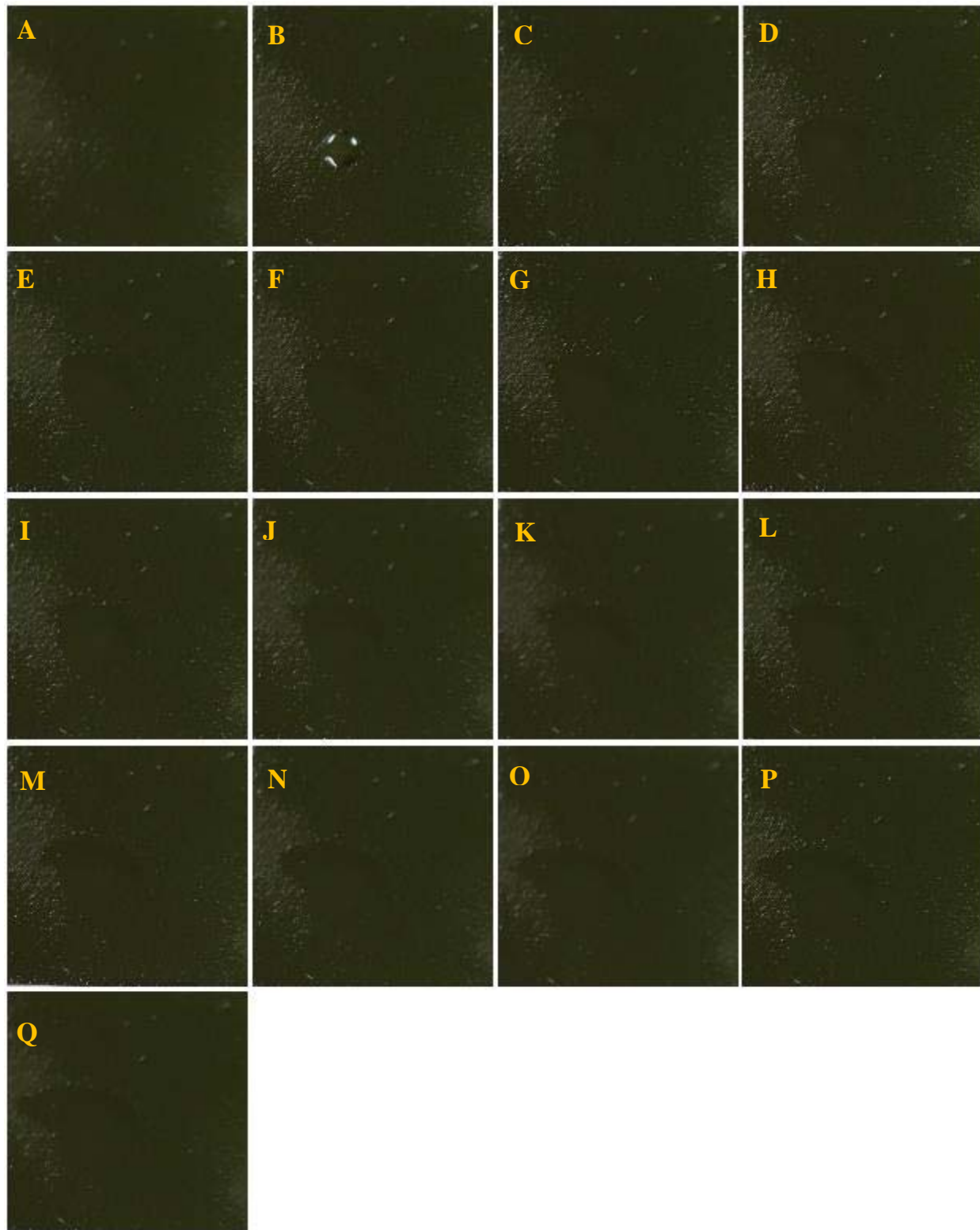
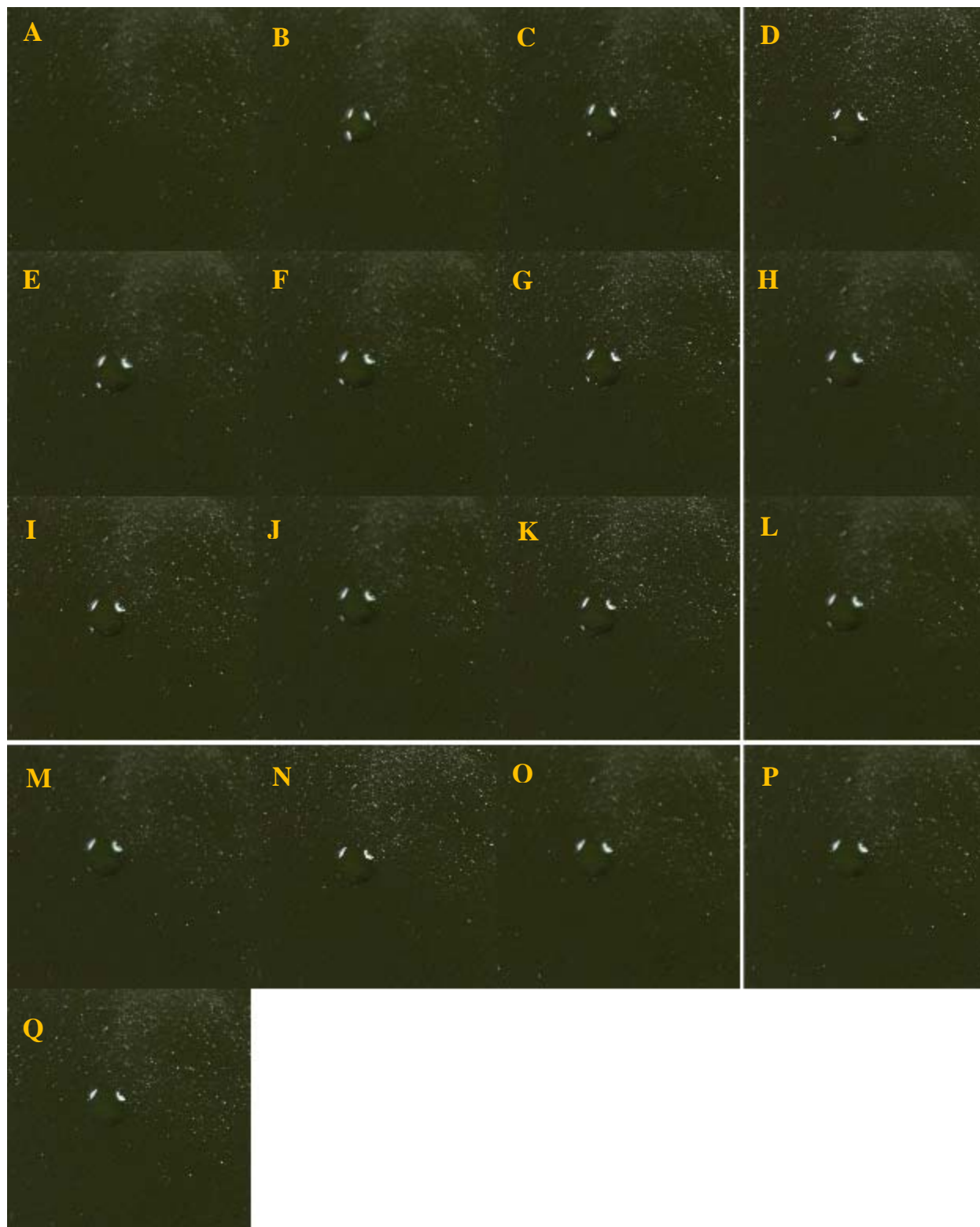


Fig. A3 — DMMP on MS0805 (neat). Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.



**Appendix B****MS0805 (SOLVENT) COUPON IMAGES**

Fig. B1 — DFP on MS0805 (solvent). Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1.0 (D), 1.5 (E), 2.0 (F), 2.5 (G), 3.0 (H), 3.5 (I), 4.0 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target. These images were collected with a glass cover in place to limit evaporation. Reflections from the cover can be seen in some images.



Fig. B2 — MES on MS0805 (solvent). Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

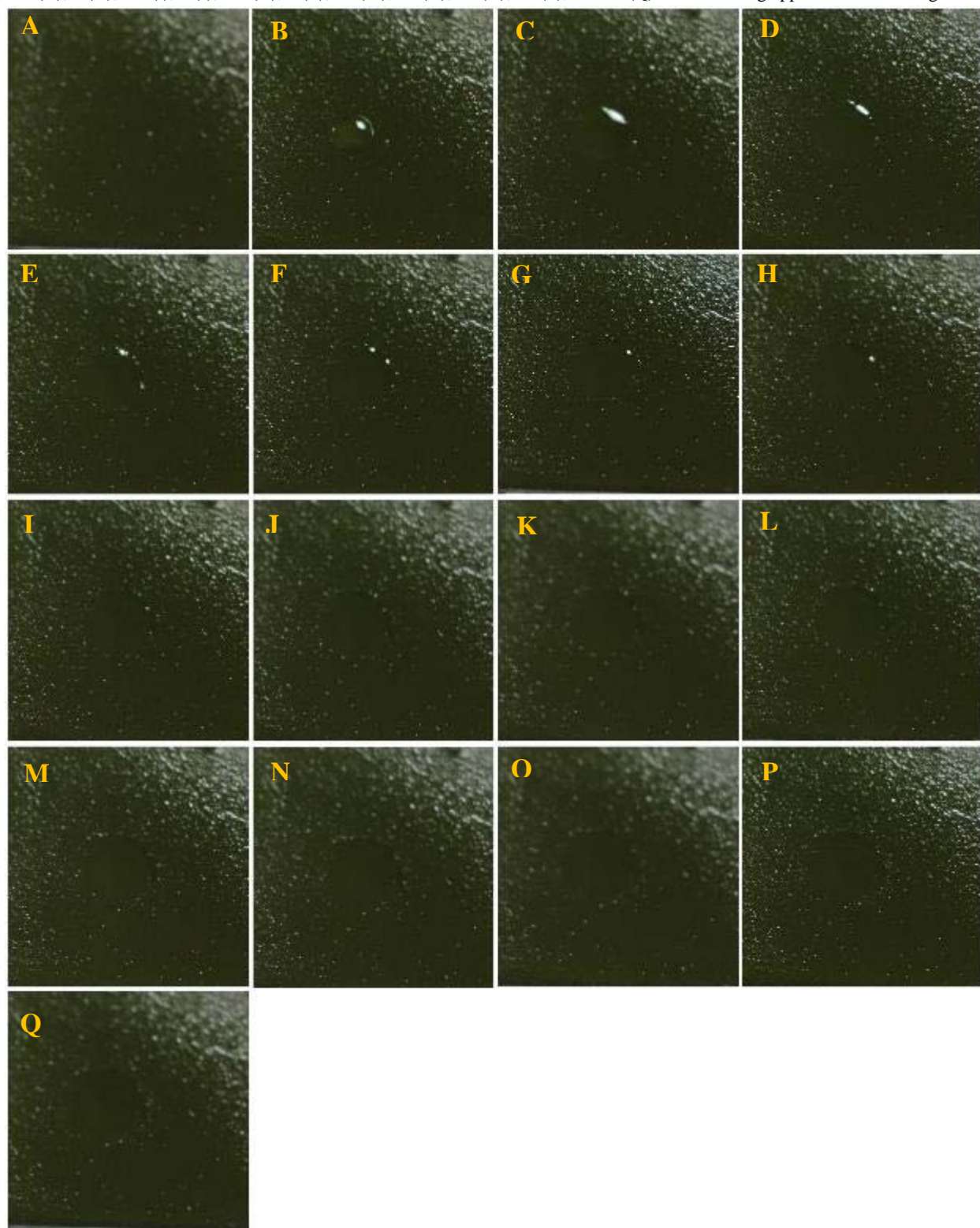
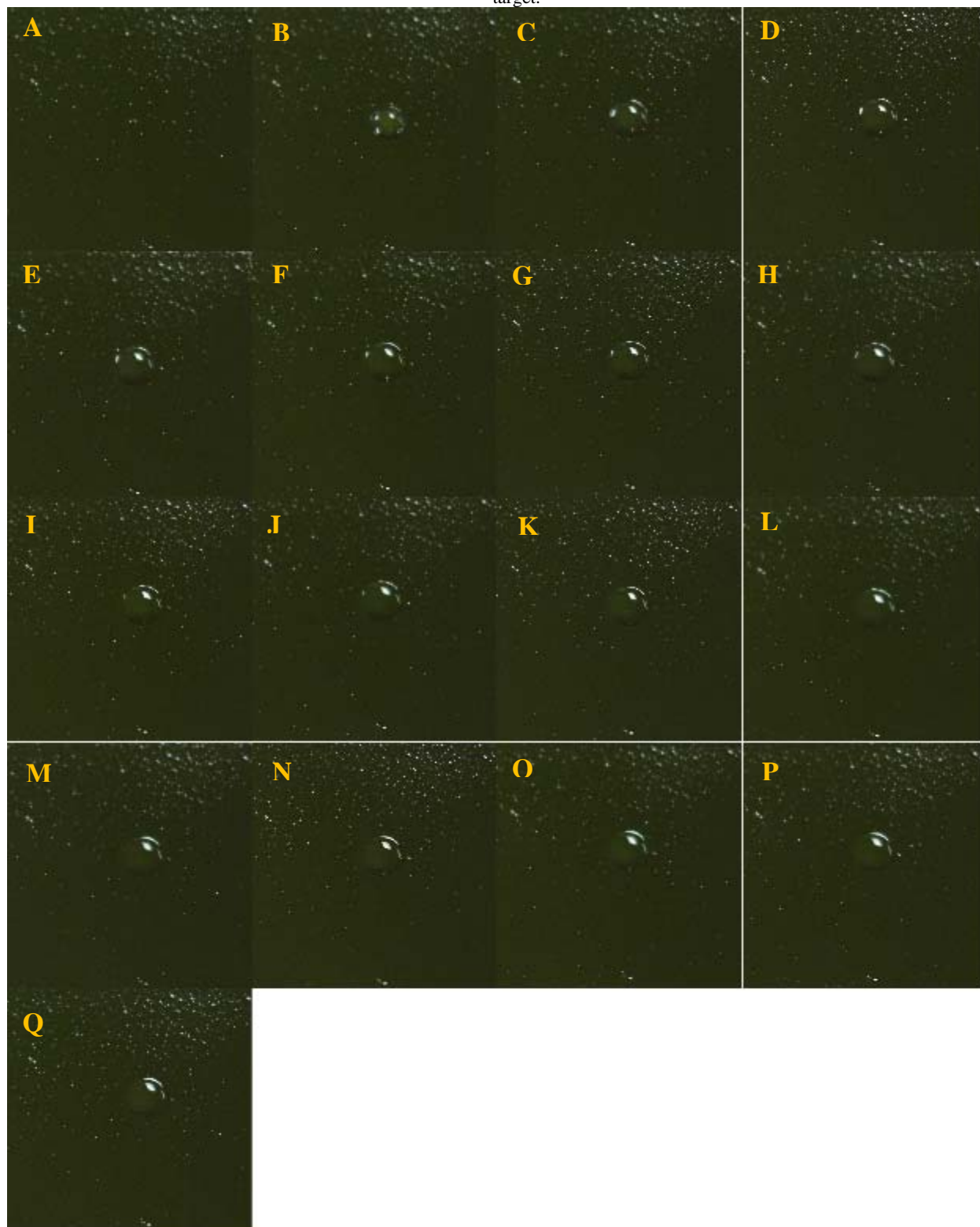


Fig. B3 — DMMP on MS0805 (solvent). Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.



**Appendix C****SO1455F (NEAT) COUPON IMAGES**

Fig. C1 — DFP on SO1455 (neat). Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1.0 (D), 1.5 (E), 2.0 (F), 2.5 (G), 3.0 (H), 3.5 (I), 4.0 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target. These images were collected with a glass cover in place to limit evaporation. Reflections from the cover can be seen in some images.

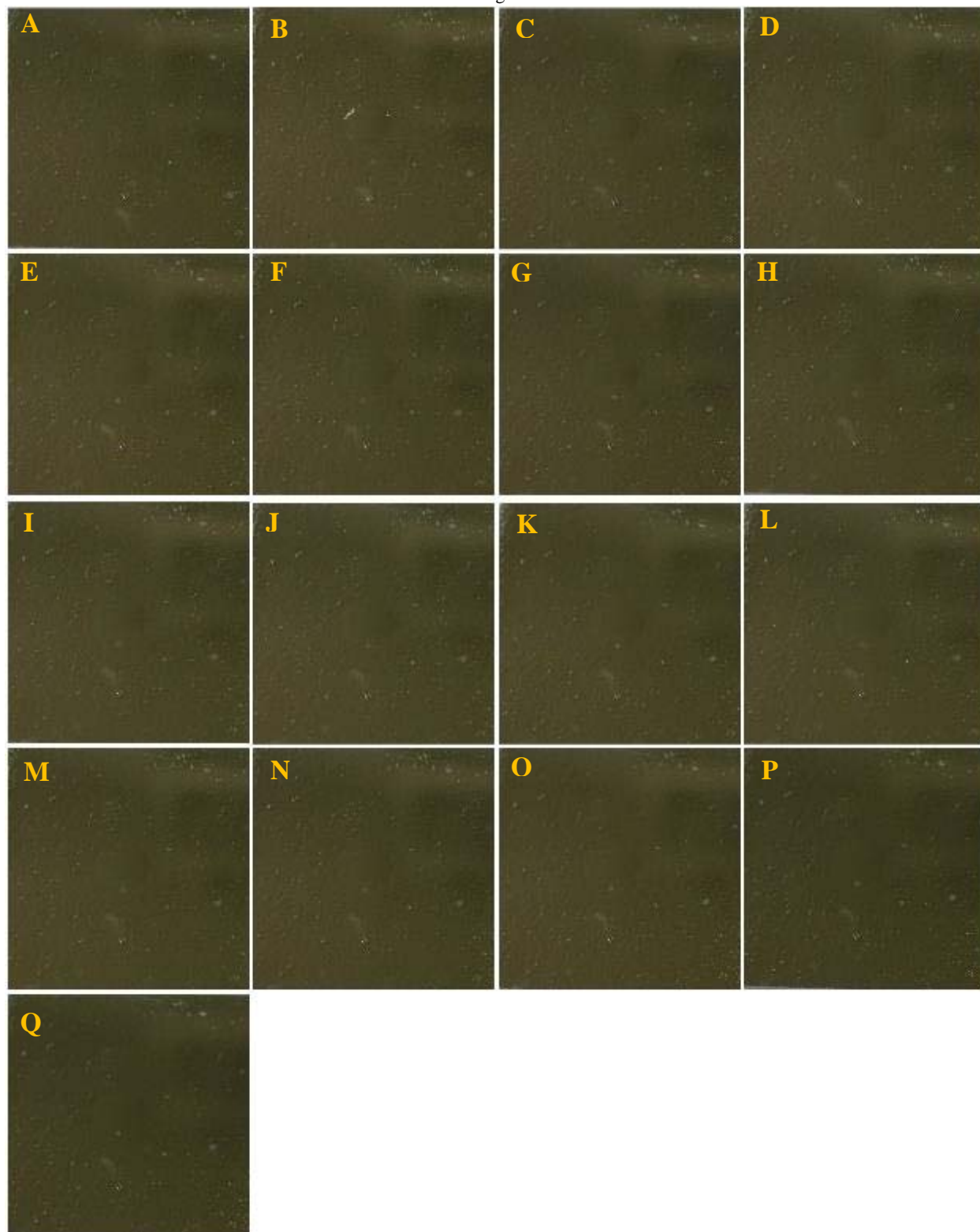


Fig. C2 — MES on SO1455 (neat). Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

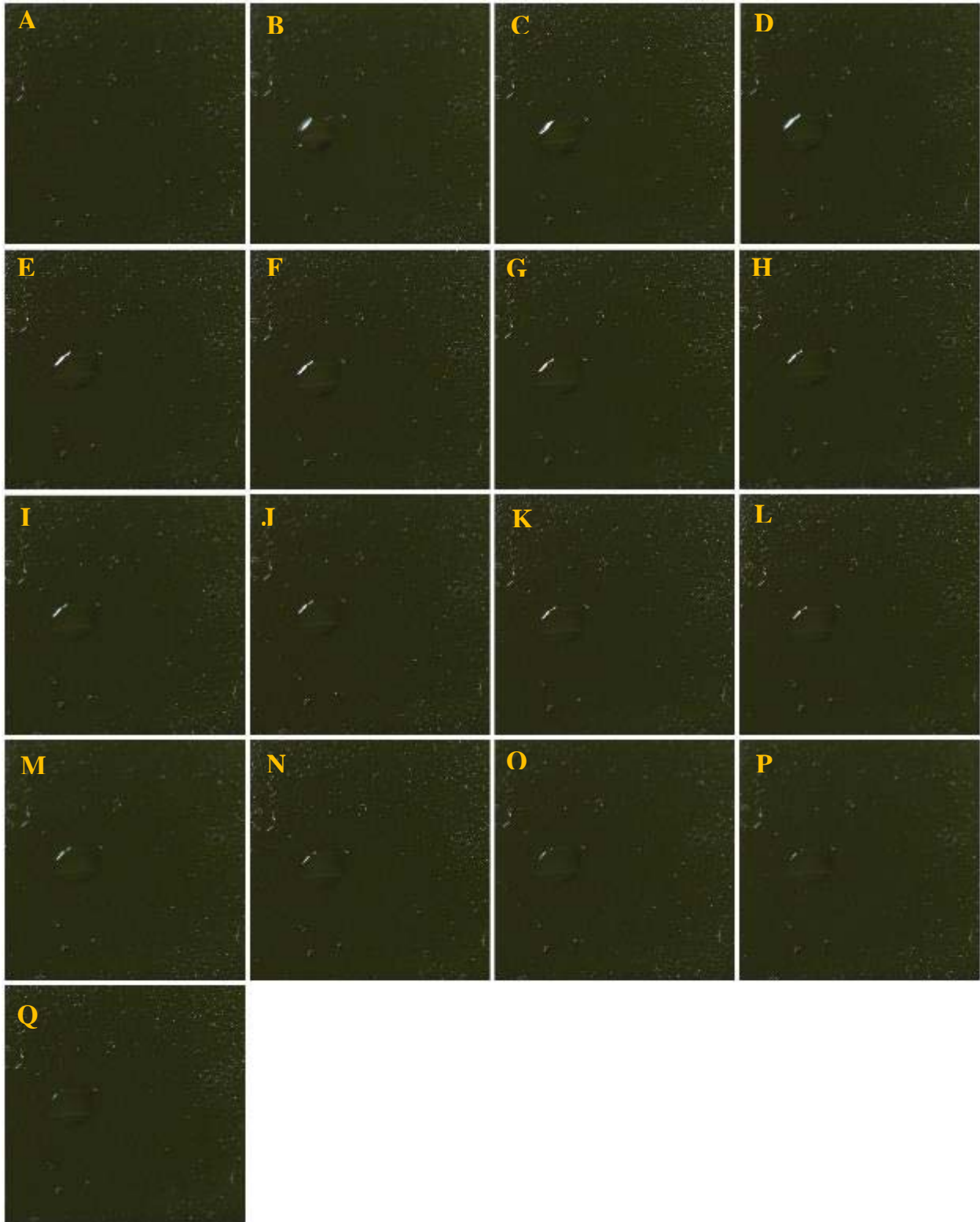
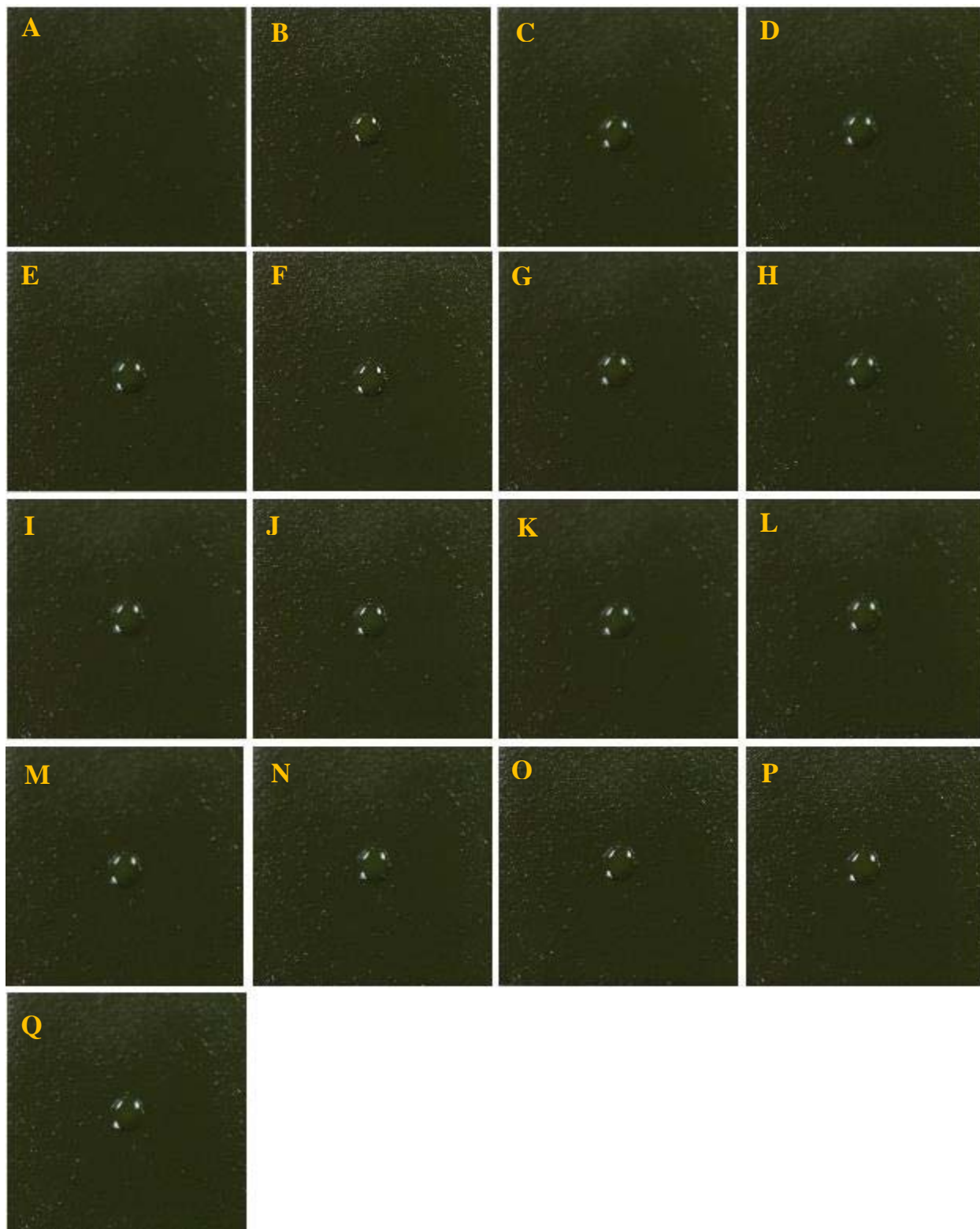


Fig. C3 — DMMP on SO1455 (neat). Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.



**Appendix D****SO1455F (SOLVENT) COUPON IMAGES**

Fig. D1 — DFP on SO1455 (solvent). Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1.0 (D), 1.5 (E), 2.0 (F), 2.5 (G), 3.0 (H), 3.5 (I), 4.0 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target. These images were collected with a glass cover in place to limit evaporation. Reflections from the cover can be seen in some images.



Fig. D2 — MES on SO1455 (solvent). Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

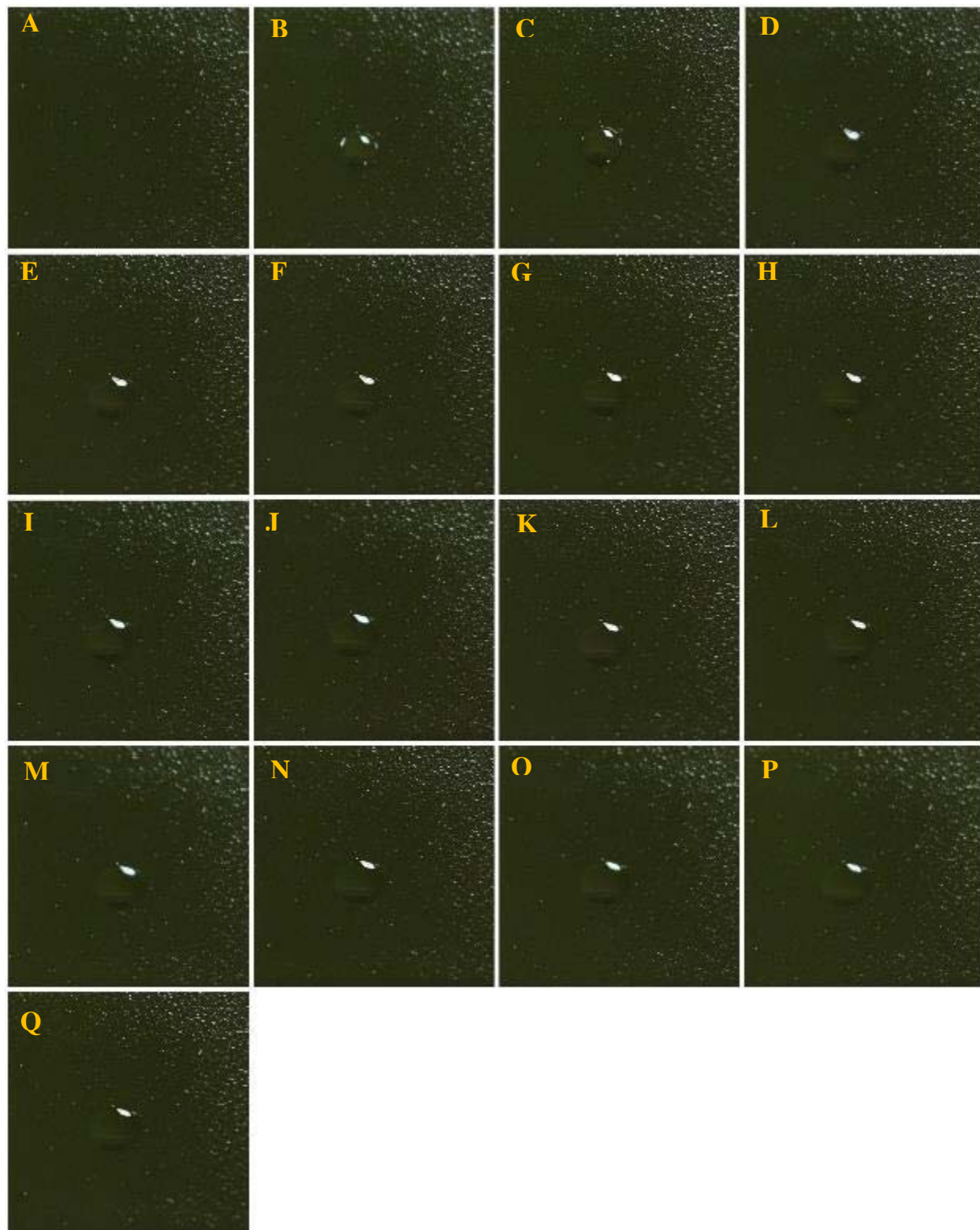
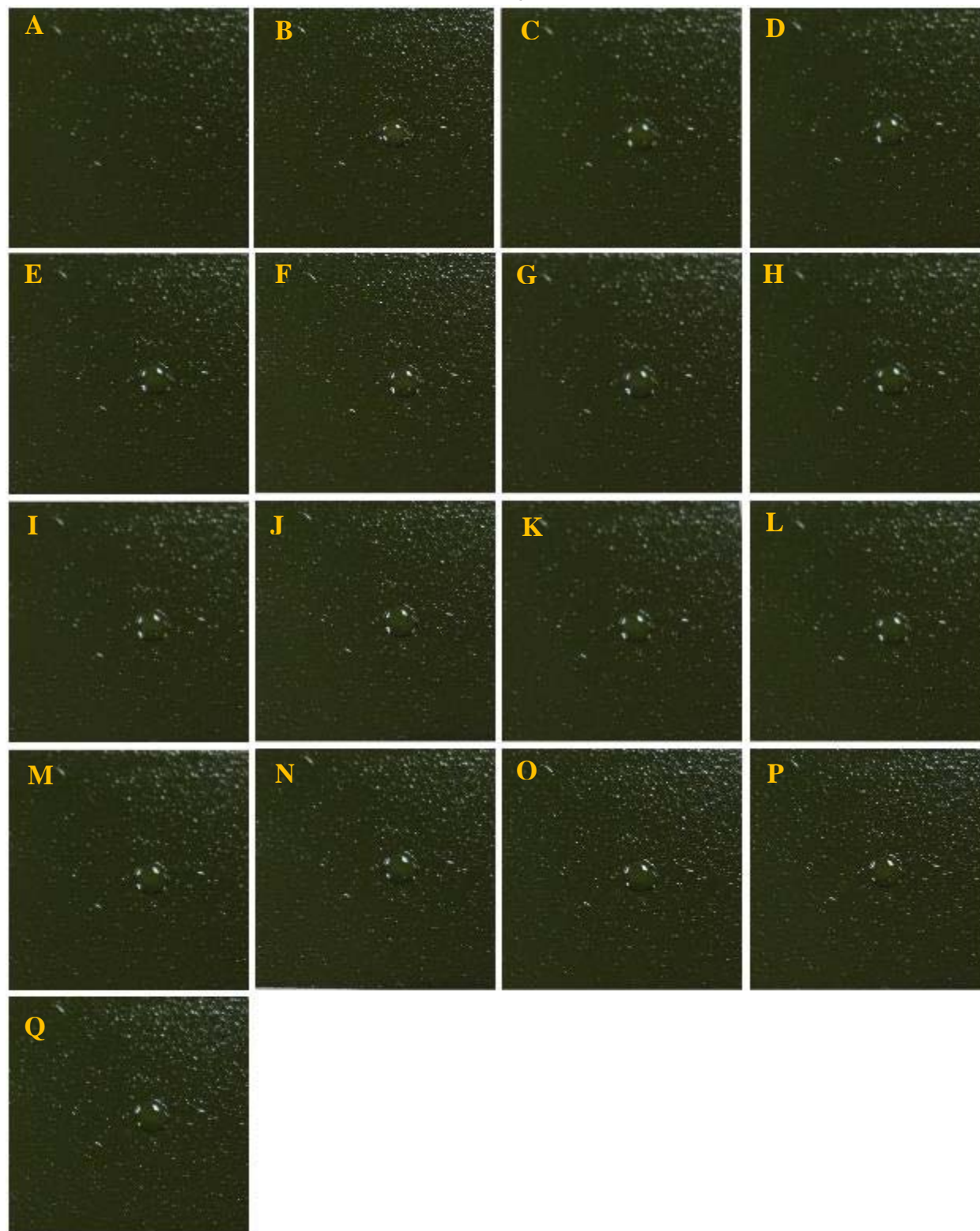


Fig. D3 — DMMP on SO1455 (solvent). Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.



**Appendix E**  
**OPTOOL COUPON IMAGES**

Fig. E1 — DFP on Optool. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1.0 (D), 1.5 (E), 2.0 (F), 2.5 (G), 3.0 (H), 3.5 (I), 4.0 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target. These images were collected with a glass cover in place to limit evaporation. Reflections from the cover can be seen in some images.



Fig. E2 — MES on Optool. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

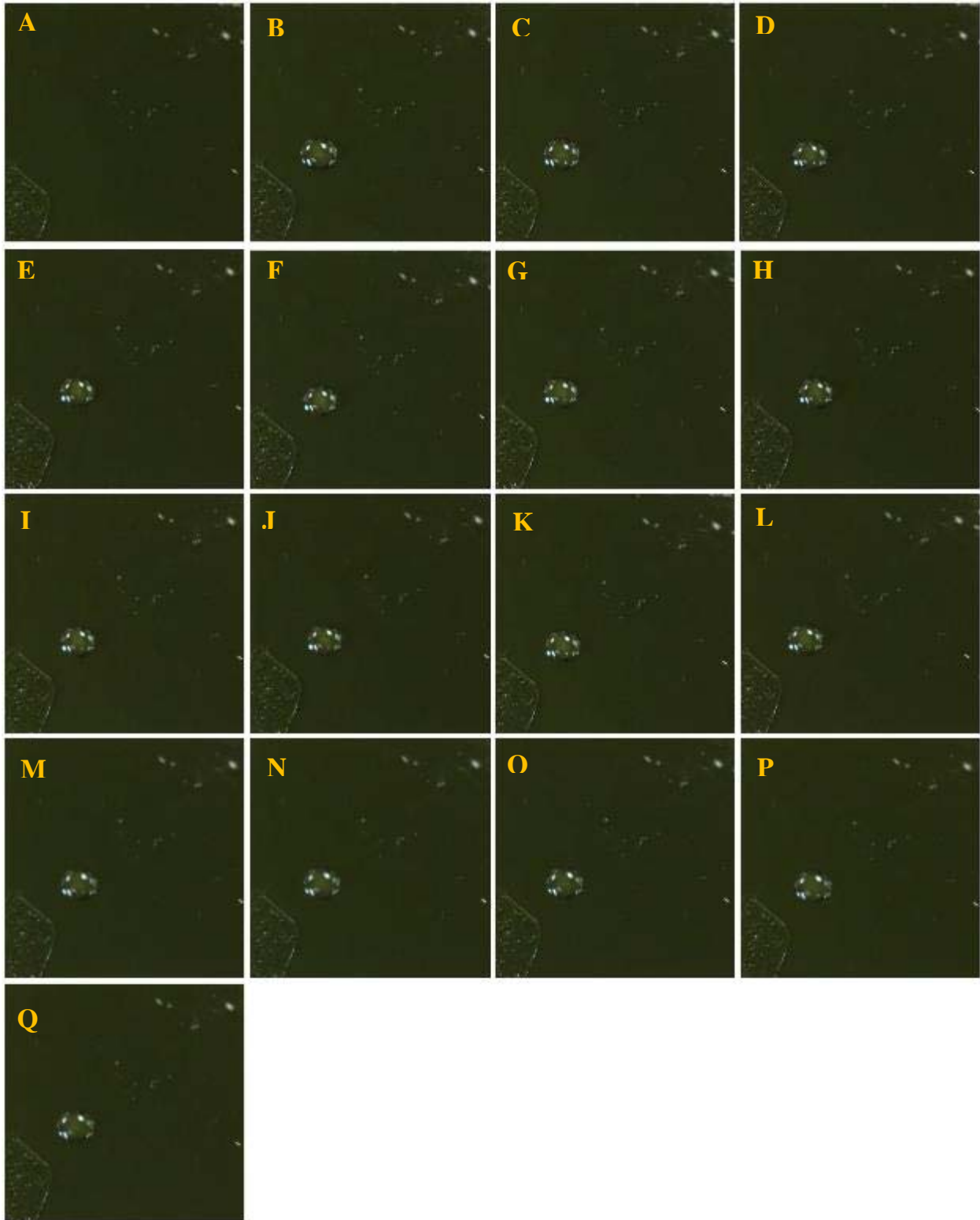
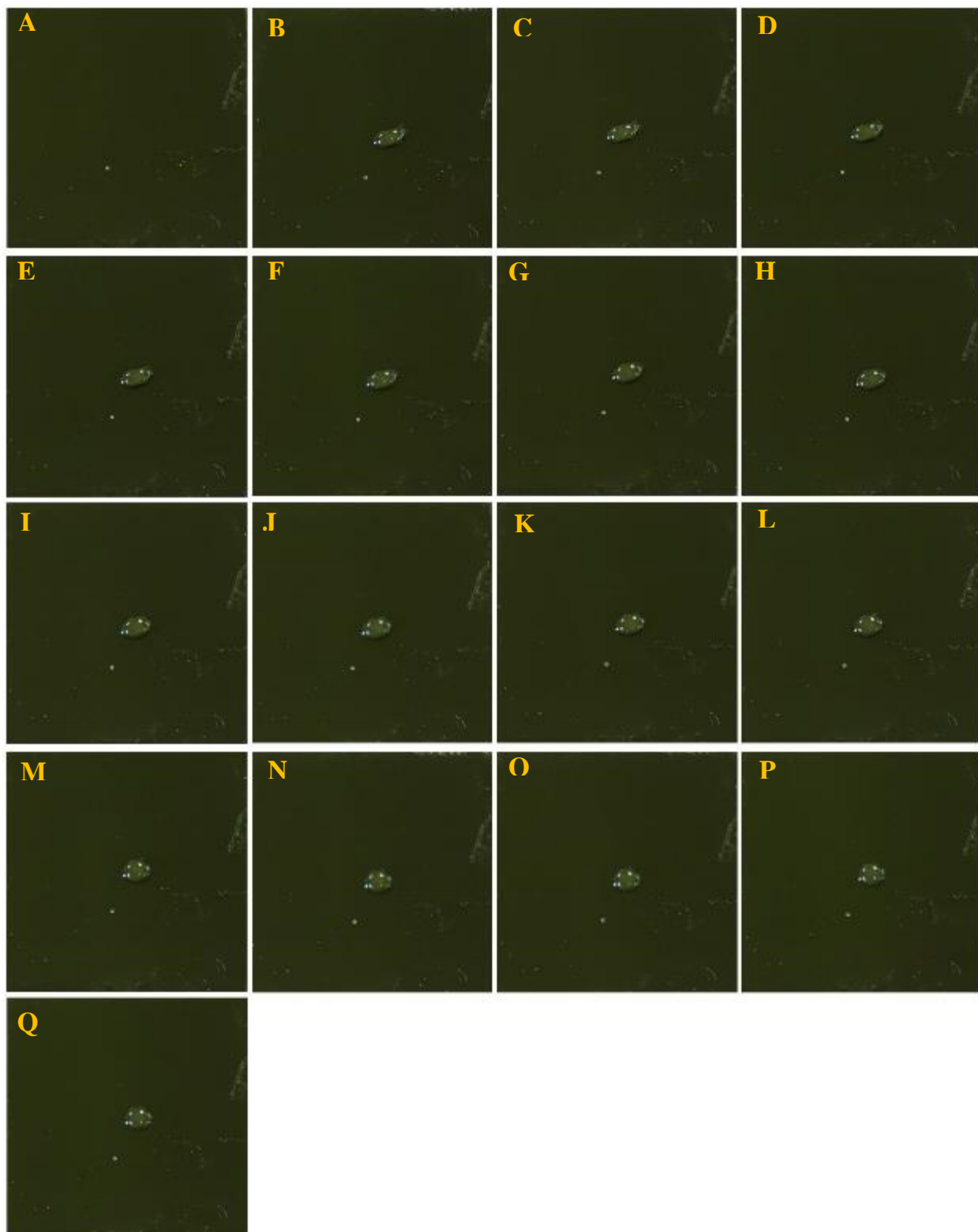


Fig. E3 — DMMP on Optool. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.



**Appendix F****MS0860 OPTOOL COUPON IMAGES**

Fig. F1 — DFP on MS0860 Optool. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1.0 (D), 1.5 (E), 2.0 (F), 2.5 (G), 3.0 (H), 3.5 (I), 4.0 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target. These images were collected with a glass cover in place to limit evaporation. Reflections from the cover can be seen in some images.

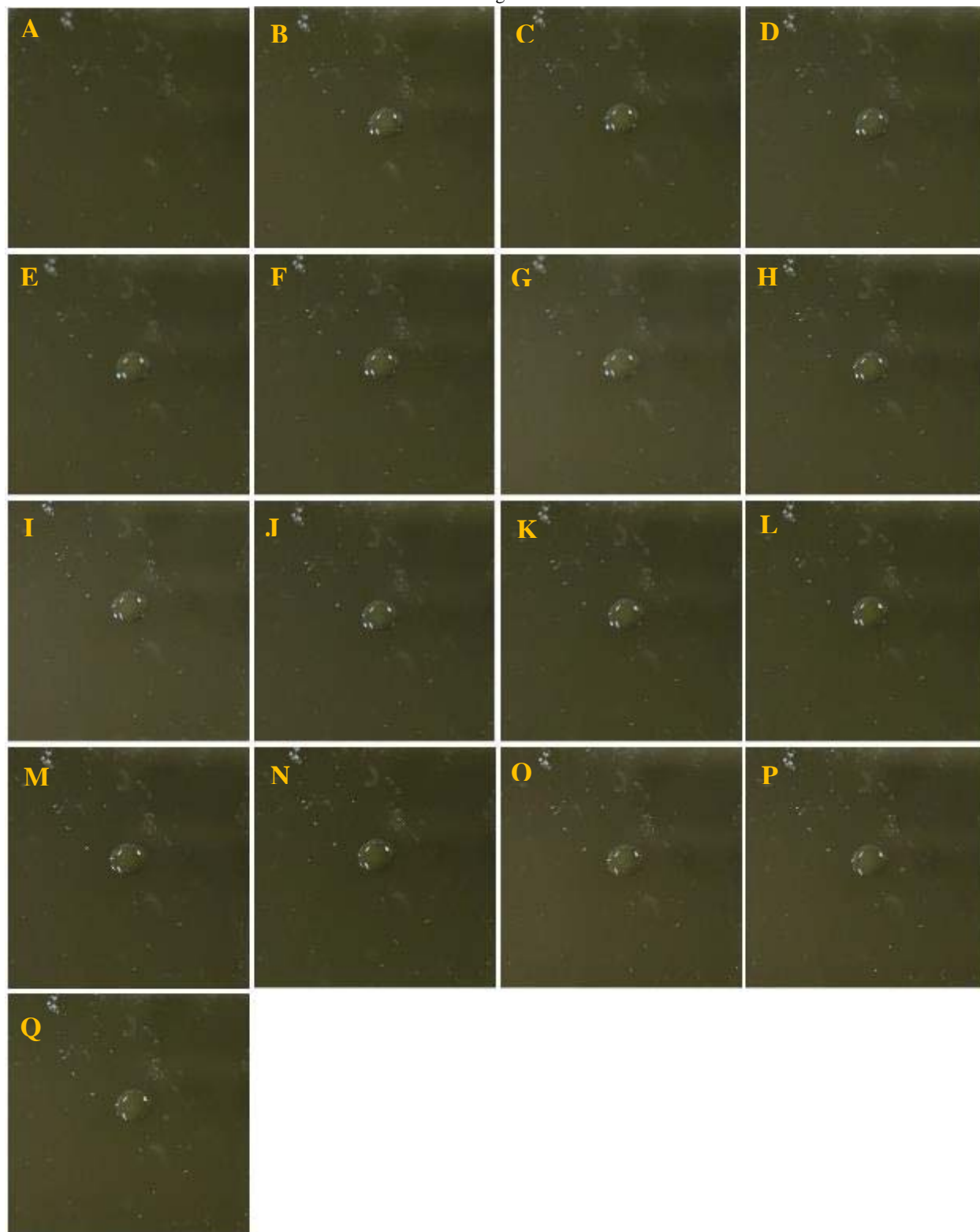


Fig. F2 — MES on MS0860 Optool. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

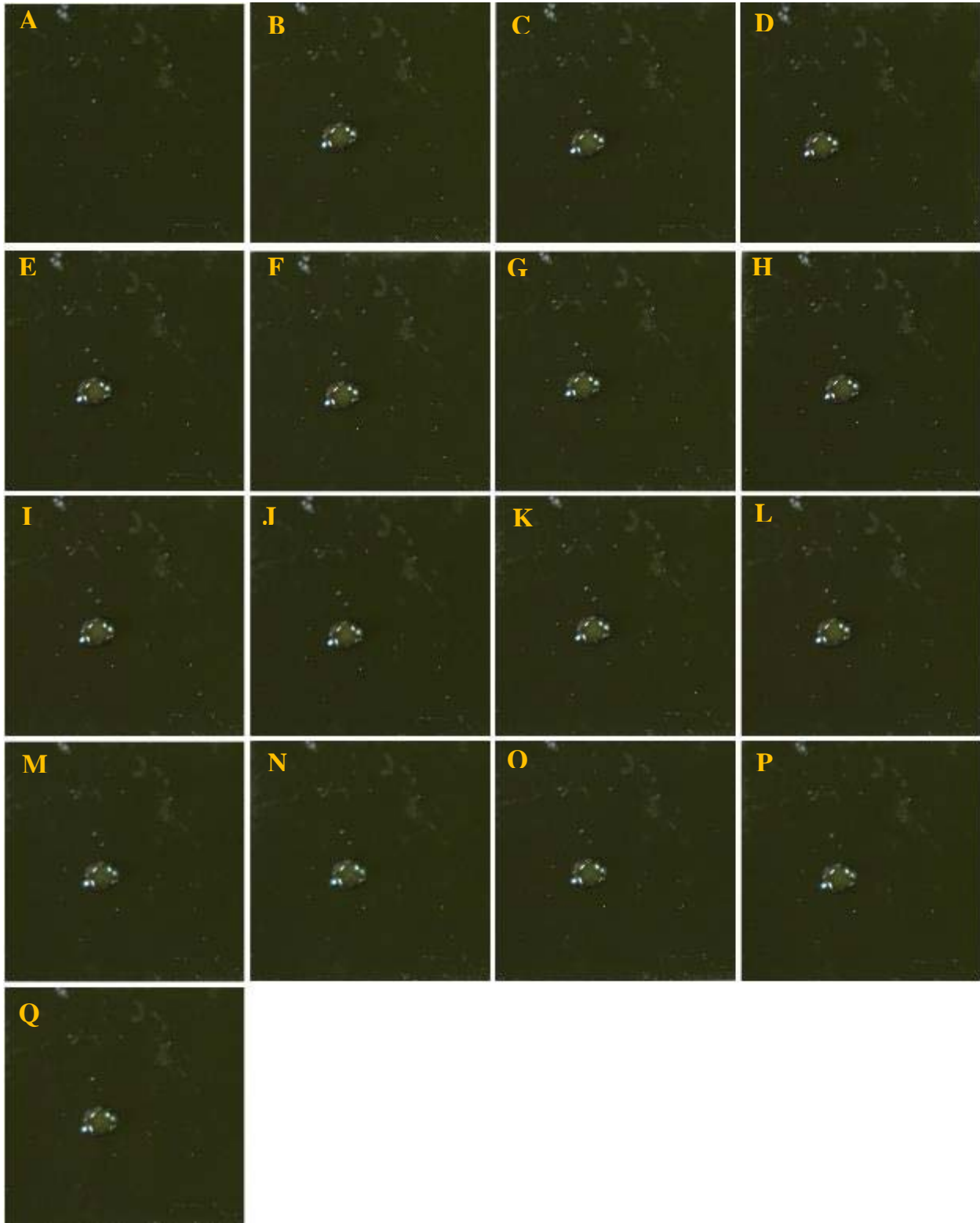
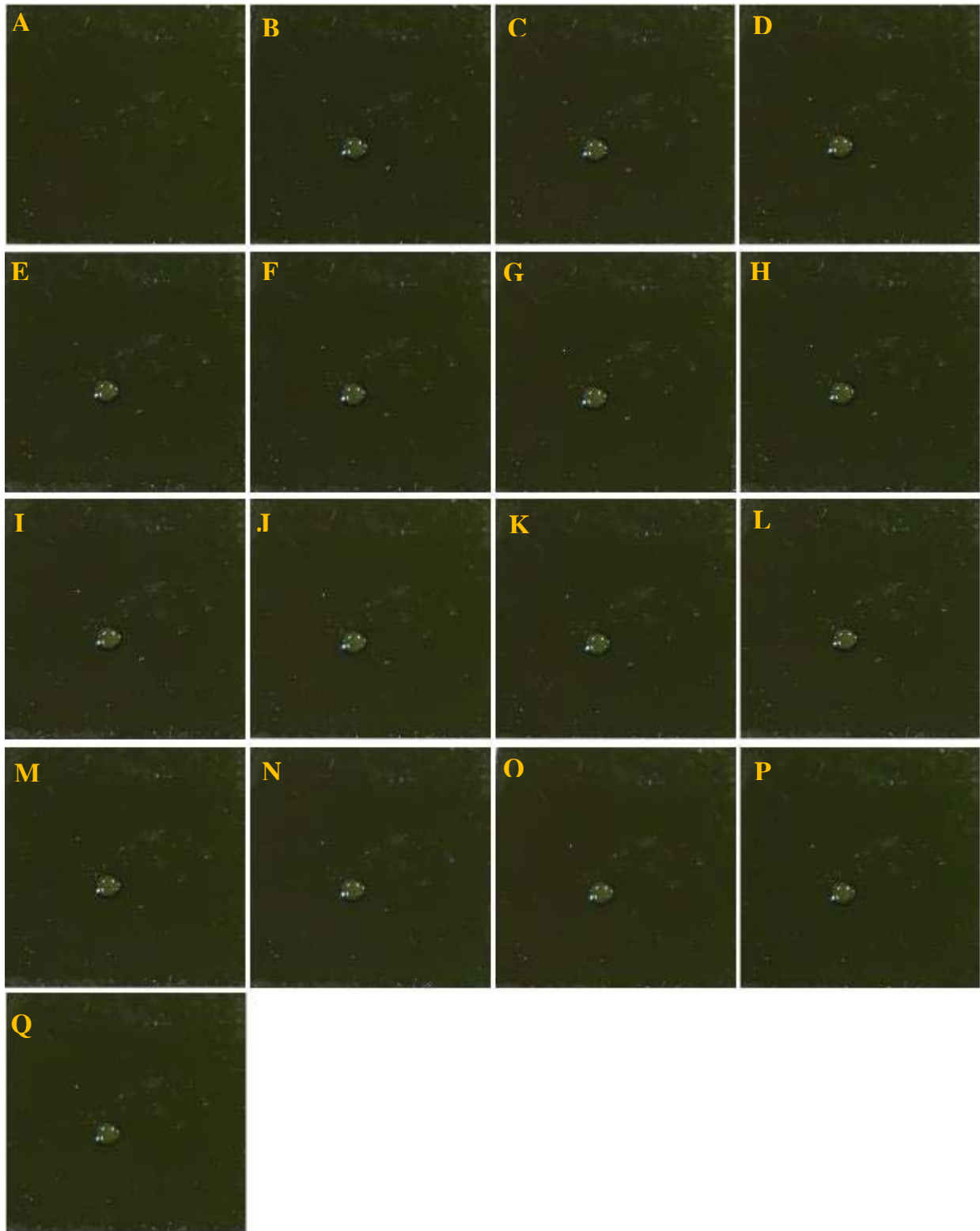


Fig. F3 — DMMP on MS0860 Optool. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.



**Appendix G**  
**PAINTED COUPON IMAGES**

Fig. G1 — DFP on paint. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1.0 (D), 1.5 (E), 2.0 (F), 2.5 (G), 3.0 (H), 3.5 (I), 4.0 (J), 4.5 (K), 10 (L), 15 (M), 20 (N), 25 (O), and 30 (P) min following application of the target. These images were collected with a glass cover in place to limit evaporation. Reflections from the cover can be seen in some images.

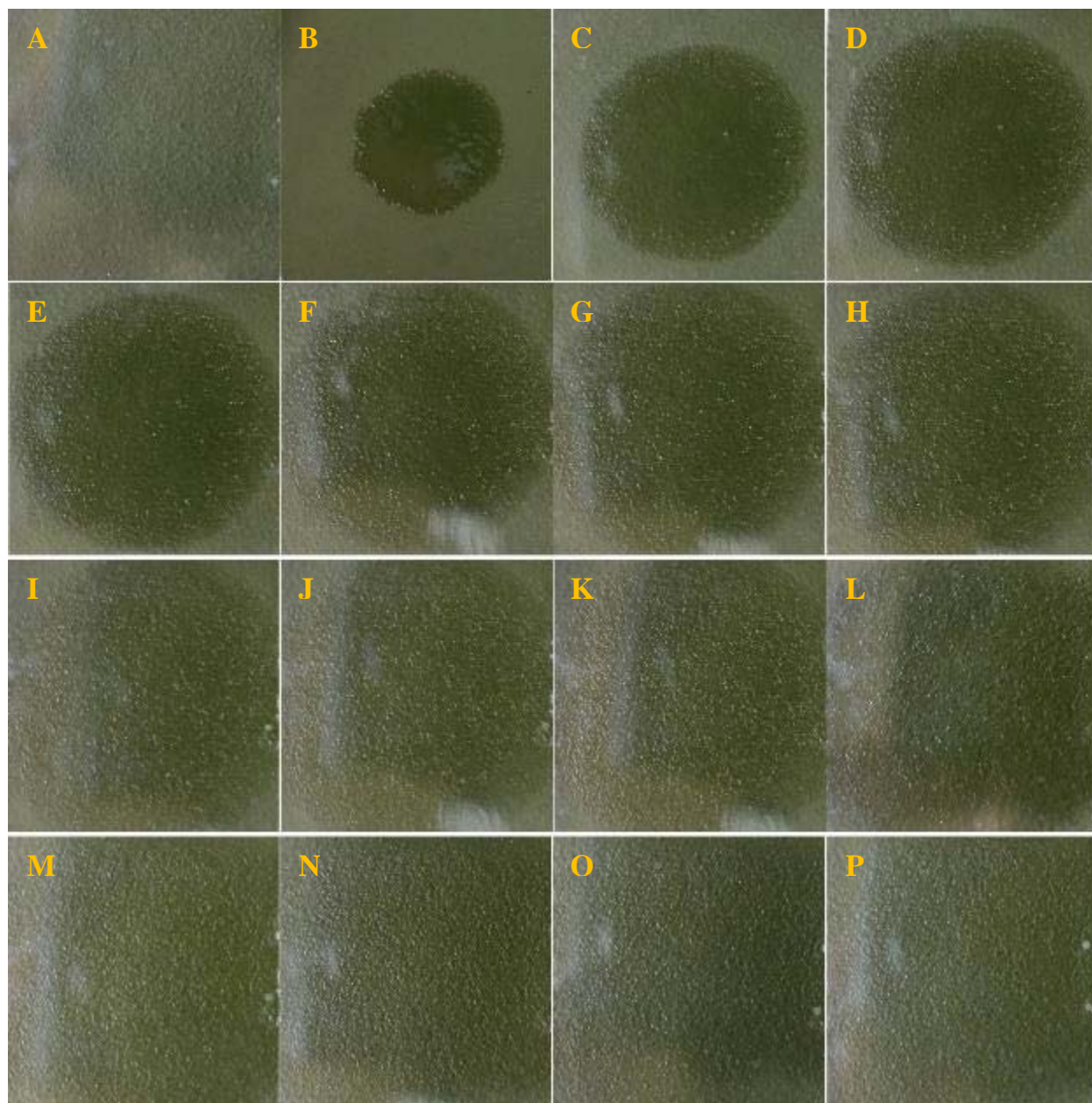


Fig. G2 — MES on paint. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

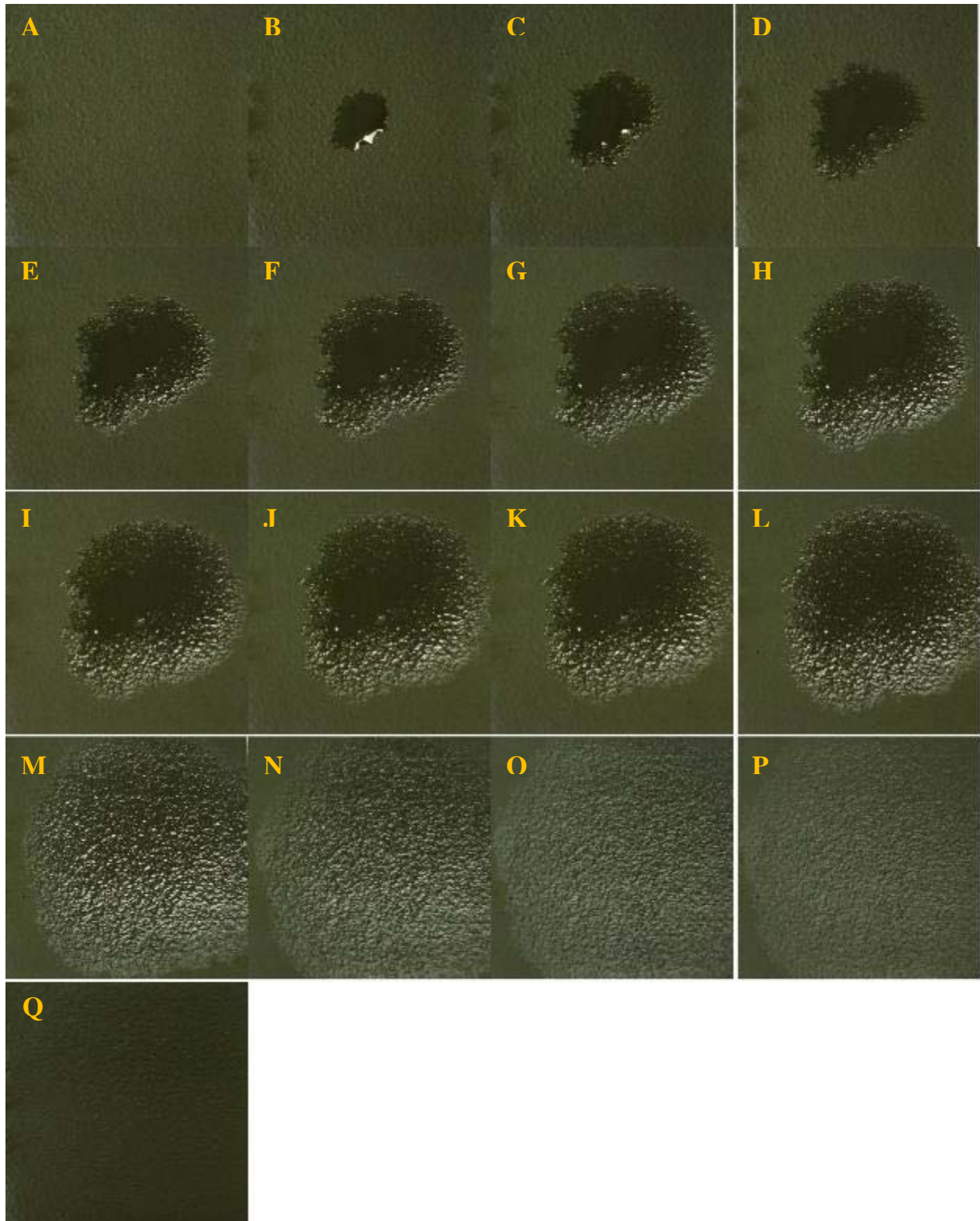
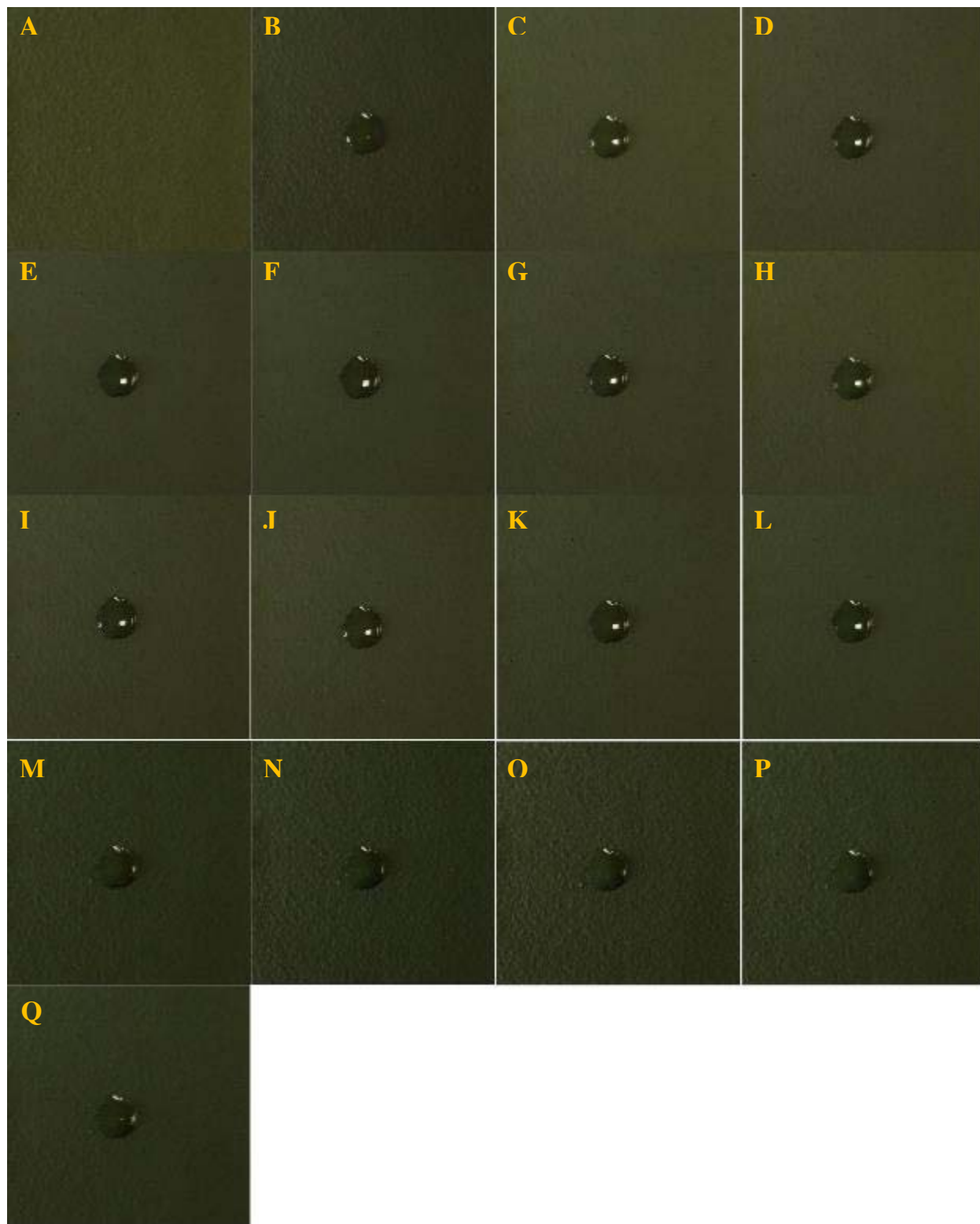


Fig. G3 — DMMP on paint. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.



## **Appendix H**

### **FOMBLIN Y LUBRICATED, PAINTED COUPON IMAGES**

Fig. H1 — DFP on Fomblin Y oiled paint. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 5.5 (M), 10 (N), 15 (O), 20 (P), 25 (Q), and 30 (R) min following application of the target. These images were collected with a glass cover in place to limit evaporation. Reflections from the cover can be seen in some images.



Fig. H2 — MES on Fomblin Y oiled paint. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 5.5 (M), 10 (N), 15 (O), 20 (P), 25 (Q), and 30 (R) min following application of the target.



Fig. H3 — DMMP on Fomblin Y oiled paint. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 5.5 (M), 10 (N), 15 (O), 20 (P), 25 (Q), and 30 (R) min following application of the target.

